AMENDMENTS

[0004] In recent years, regarding the methods for producing nitrogen, a method that uses an adsorbent preferentially adsorbing oxygen to produce high purity nitrogen gas from a gas mixture of oxygen and nitrogen, such as the air, with a PSA method has been widely adopted. The carbon molecular sieve (CMS), as its name indicates, is an activated carbon that has the function of molecular sieving, and features with a smaller mean pore size and a sharper pore size distribution as compared with general activated carbon. Since the pore size of CMS is very close to the molecular size of the adsorbate, the adsorption rates are lower for certain adsorbent/adsorbate combinations. For example, in the case that a nitrogen-rich gas is obtained from a gas mixture of oxygen and nitrogen like the air, the CMS preferably has an adsorption rate for nitrogen much lower than that for oxygen because of the difference between the molecular sizes of oxygen and nitrogen.

[0007] To improve the performance of a nitrogen PSA apparatus, many techniques are disclosed focusing on both the adsorbent and the PSA process itself. The correlation between the adsorbent and the nitrogen PSA apparatus is disclosed in Japanese Patent Publication No. Sho 54-17595, wherein the nitrogen PSA operation uses a coke molecular sieve obtained by introducing a hydrocarbon and decomposing it with pyrolysis to release carbon, and depositing the released carbon in the pores of coke. The nitrogen PSA operation features ~~with~~ that a raw gas is introduced with a flow-through rate of $0.01{\sim}0.04Nm^3$ per second with $1m^3$ of the coke molecular sieve.

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[0010] Japanese Patent Application Laid Open No. Hei 3-232515 describes the use of a CMS

that ~~have~~ has adsorption amounts of 20~27mg/g and 1~6mg/g for oxygen and nitrogen,

respectively, under an adsorption pressure of 245kPa (gauge pressure) after 1 minute, and has an

adsorption amount of 22~34mg/g for the two at equilibrium. The application also disclosed that

the adsorption time in the high-pressure adsorption step is 130~300 seconds and the outflow rate

(L/min) of the nitrogen product is 0.1~3.0 times the volume (L) of the adsorbing column in the

PSA operation. In this application, the properties of the used adsorbent and the limitation of the

range of the ratio of "the product outflow rate to the volume of the adsorbing column", which is

the characteristic value of the PSA operation, are decided according to the concentration of the

oxygen gas contained in the nitrogen product.

[0029] Under the aforementioned conditions, some carbon molecular sieves (CMS) are prepared

by depositing the carbon produced by benzene pyrolysis onto the activated carbon material. By

adjusting the treating time of carbon deposition, six CMS adsorbents having different times for

adsorbing an amount of 50% of the adsorbed amount at equilibrium (i.e., different adsorption

rates) are fabricated experimentally, including CMS-A, CMS-B, CMS-C, CMS-D, CMS-E and

CMS-F. For these CMS adsorbents, the time "TO" needed to adsorb an oxygen amount of 50%

of the adsorbed amount of oxygen at equilibrium, the time "TN" needed to adsorb a nitrogen

amount of 50% of the adsorbed amount of nitrogen at equilibrium, and the ratio (separating ratio)

"TN/TO" are listed in Table 1. The CMS is used to adsorb the gas at 25°C under an initial

pressure of 26.7kPa (absolute pressure) in the commercially available apparatus "Belsoap 28" for measuring the adsorbed amounts. The gas ~~in~~ is introduced under specific measuring conditions, including an adsorption temperature of 25°C and an initial pressure of 26.7kPa (absolute pressure). The values measured with the adsorption amount measuring apparatus, Belsoap 28, are listed in Table 1.

~~[11]~~

[0031] In the case that two adsorbing columns are used, generally, when an adsorption step is performed in one column, a regeneration step is performed in the other. Therefore, by alternatively and periodically switching the adsorption step and the regeneration step, the product ~~are~~ is obtained continuously. A schematic diagram of a nitrogen PSA apparatus of this invention is illustrated in FIG. 2 for explaining the nitrogen-producing method of this invention. At first, the raw air is compressed to a predetermined pressure, such as a maximal pressure of 786kPa (gauge pressure), by using an air compressor 13, and then supplied to adsorbing columns 11 and 12 through an air dryer 14. The adsorbing columns 11 and 12 are filled with CMS.

[0032] When an adsorption step is performed in the adsorbing column 11 and a regeneration step is performed in the adsorbing column 12, the raw air is supplied to the adsorbing column 11 through the valve 17 after being compressed by the air compressor 13 and conducted through the air dryer 14 to be dried with water removal. The compressed raw air supplied into the adsorbing column 11 contacts with the CMS filled in the adsorbing column 11, wherein the oxygen is

selectively adsorbed and removed. Nitrogen that is more difficult to adsorb as compared with

oxygen is collected from the valve 23 and stored in the product tank 29 before being supplied to

users.

[0056] · PSA process: air pressurization   adsorption   equalization/depressurization

depressurization regeneration   purging regeneration   equalization/pressurization.   When the half

cycle time is 90 seconds, for example: from air pressurization to adsorption: 85 seconds

[0064] The experiments are conducted under the aforementioned operating conditions, wherein a

suitable half cycle time is selected for each kind of adsorbent. For each kind of adsorbent, the

nitrogen recovery ratio η [%] and the unit collection rate w0 [Nm³/h/ton] (w0 = (nitrogen

production rate) / (amount of adsorbent filled in one column)) that indicates the performance of

the PSA process are listed in Table 2.

[12]

[0065] The results in Tables 1 & 2 obviously implies that the CMS that adsorbs an oxygen

amount of 50% of the saturated oxygen adsorption amount with a period TO shorter than 10

seconds can make a higher collection rate in the PSA process. The adsorbents CMS-C, D, E & F,

which having have adsorption times TO from 5.8s to 6.9 9.6s as shown in Table 1, all have

relatively higher collection rates. That is, the adsorbents CMS-C, D, E & F that have adsorption

times (TO) for adsorbing 50% of the saturated oxygen adsorption amount shorter than 10

seconds have collection rates about 20% higher than those of CMS-A & B that have adsorption

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times (TO) longer than 10 seconds. That is, the performance variation of the nitrogen PSA apparatus is obviously large with only a variation of 1~2 seconds in the adsorption time "TO" needed for 50% of the saturated adsorption amount. Therefore, it is confirmed that the time "TO" needed to adsorb an oxygen amount of 50% of the saturated oxygen adsorption amount is preferably 5~10 seconds.

[0074] Now, for the six kinds of adsorbents mentioned above, the results of Example 1 are substituted into the equation above to obtain the air-processing rate per unit adsorbent weight, wherein the nitrogen PSA apparatus illustrated in FIG. 2 is used to perform experiments in Example 1. The results are listed in Table 3. In addition, the weight of the filled adsorbent is one ton.

[14]

[0081] Analogously, CMS-D are taken as a standard, the adsorbents that have nitrogen-collecting rates higher than that of CMS-D are CMS-E and F. However, the nitrogen-collecting rate of CMS-E is increased by +15% with only an increase of +9% in the air processing rate, while the nitrogen-collecting rate of CMS-F is increased by only +7% even though the air processing rate is increased by +11%. For CMS-C, the nitrogen-collecting rate is –4% lower but the air-processing rate is –12% lower, which indicates a better efficiency in product collection. Therefore, when the oxygen concentration is10000ppm, the preferable adsorbents are CMS-C, D & E.

[0082] The comparison made above is an example that uses CMS-D as a standard, so CMS-C, D & E are considered superior at any nitrogen purity. However, if CMS-E is taken as the standard, the air-processing rate variations of CMS-D are –8%, –2% and –2%, and the nitrogen-collecting rate variations are –13%, –11% and –14% as the nitrogen purity is 99%, 99.9% and 99.99%, respectively, which means that the efficiency of nitrogen recovery is remarkably lower. On the contrary, with CMS-E as a standard, the air-processing rate variations of CMS-C are –20%, –20% and –13%, and the nitrogen-collecting rate variations are –17%, –17% and –8% as the nitrogen purity is 99%, 99.9% and 99.99%, respectively, which means that the efficiency in nitrogen collection is higher. Therefore, the preferable adsorbents are CMS-C and E. Moreover, the ratio TN (for N_2) / TO (for O_2) suitably serves as the indicator of the property of the adsorbent relating with the air-processing rate since CMS-F that has a sufficiently small TO value (i.e., a sufficient adsorption rate) but an insufficient ratio of TN to TO, as shown in Table 1, is not good in the results of PSA evaluation shown in Tables 2 & 3. Accordingly, the air-processing rates of CMS-F, 500Nm³/h/ton, 570Nm³/h/ton and 690Nm³/h/ton, are taken as the upper limits as the oxygen concentrations are 100ppm, 1000ppm and 10000ppm, respectively.

[0083] Moreover, when the adsorbent ~~in claim 1~~ of this invention is used, PSA performance can be obtained with the numerical limits described ~~in claims 2 and 3~~ above as the oxygen concentrations in nitrogen are 100ppm, 1000ppm, or 10000ppm. However, for commercial apparatuses, a single apparatus is not used to produce nitrogen products of various concentrations and is constituted so that the specific concentration required by the customers can be generated.

Therefore, by comparing the specified concentration and those claimed in this invention, the concentration condition of the nitrogen product produced by the commercial apparatus conflicts with the restricted range of this invention. Besides, in the domains of intermediate concentration, the process conditions are derived by connecting the two points at 100ppm and 1000ppm, respectively, with a line and by connecting the two points at 1000ppm and 10000ppm, respectively, with a line, and using an interpolation method.